Report Documentation Page		Form Approved OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **2007**	2. REPORT TYPE	3. DATES COVERED **00-00-2007 to 00-00-2007**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Giant Enhancement in UV Response of ZnO Nanobelts by Polymer Surface-Functionalization	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Georgia Institute of Technology,School of Materials Science and Engineering,Atlanta,GA,30332**	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**2**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Giant Enhancement in UV Response of ZnO Nanobelts by Polymer Surface-Functionalization

Chang Shi Lao,[†] Myung-Chul Park,[‡] Qin Kuang,[†] Yulin Deng,[‡] Ashok K. Sood,[§] Dennis L. Polla,[#] and Zhong L. Wang*,[†]

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0620, Magnolia Optical Technologies, Inc., 52-B Cummings Park, Suite 314, Woburn, Massachusetts 01801, and Defense Advanced Research Projects Agency/Microsystems Technology Office (DARPA/MTO), 3701 North Fairfax Drive, Arlington, Virginia 22203-1714

Received July 13, 2007; E-mail: zhong.wang@mse.gatech.edu

Zinc oxide (ZnO) is one of the most important nanomaterials for nano-optoelectronics,[1] sensors,[2] transistors,[3,4] and nanopiezotronics.[5,6] Because of the unique piezoelectric and semiconducting dual properties, ZnO nanowires (NWs) and nanobelts (NBs) are the fundamental material for nanogenerators,[7−9] which convert mechanical energy into electricity. With a band gap of ∼3.4 eV and an exciton binding energy of 60 meV, ZnO has huge promise for optical applications, such as UV detection.[10] However, because of the presence of point defects and confined dimensionality, the UV sensitivity of ZnO NWs and NBs is limited.

In this paper, we demonstrate that the UV response of a ZnO NB based sensor has been enhanced by close to 5 orders of magnitude after functionalizing its surface with a polymer that has a high UV absorption ability. This giant enhancement in photoconductance is attributed to the energy levels introduced by the polymer lying in the corresponding band gap and in the conduction band of ZnO, which served as a "hopping" state and increased the excitation probability of an electron to the conduction band. This exciting discovery will greatly impact the applications of ZnO NWs/NBs for UV detection.

The device fabrication was achieved using e-beam lithography and focused ion beam (FIB) microscopy.[11] Surface functionalization is one of the widely used methods to enhance the electric transport properties of different 1D nanostructures.[12] Because of the special physical and chemical properties of the attached chemical species, devices based on ZnO NWs/NBs demonstrate unique and interesting properties.[13] In this paper, a layer-by-layer self-assembly method was used for manipulating and functionalizing polymers onto the surface of ZnO NBs.[14] In general, since the functional polymers used for UV sensing was negatively charged, a positively charged polymer, poly(diallyldimethylammonium chloride) (PDADMAC), was chosen to assist the electrostatic assembly of the negatively charged polymer. Surface charge of ZnO NBs is negative in aquatic solution according to ζ-potential measurement. Prior to surface coating, the ZnO NBs used in the devices were cleaned with oxygen plasma to remove surface chemical residuals and other contaminants before testing or polymer functionalization. For a bare ZnO NB, PDADMAC was first adsorbed onto its surface by electrostatic attraction force between the negative surface charges of ZnO and positive charges of PDADMAC. Then, the ZnO NB was immersed in an anionically charged polymer solution of choice, which was adsorbed on the ZnO NB owing to the electrostatic force from the cationically charged PDADMAC molecules.

Different kinds of polymers with different UV absorption abilities and wavelengths were used in the experiment to test their effects

[†] School of Materials Science and Engineering, Georgia Institute of Technology.
[‡] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology.
[§] Magnolia Optical Technologies, Inc.
[#] DARPA/MTO.

on enhancing UV response of the ZnO NB, including polystyrene sulfate (PSS), poly(styrene-co-maleic acid) (PS-co-MAc), anionically charged poly(N-isopropylacrylamide) (PNIPAM), and carboxymethylcellulose (CMC). For the layered coating, these polymers are all negatively charged or modified to possess negative charges. A scanning electron microscopy (SEM) image of these functionalized ZnO NBs is shown in the inset of Figure 1b. The blur edge of NBs in the figure indicates successful coating of polymers onto the NBs.

Ultraviolet characteristics of the polymer functionalized ZnO NB base devices were tested to investigate their electric transport under UV illumination. Figure 1a is the photoconductance response of the single NB devices fabricated using ZnO NBs functionalized with different polymers, and the data are plotted for the ratio of the conductance measured when the UV was on (G) and off (G_0). The UV source used in the experiment had a wavelength distribution around 280 nm. The conductance of uncoated ZnO NB devices (green line) increased for 2.8 times upon UV illumination. The conductance of the PS-co-MAc-coated NB (dark line) increased for 50 times upon UV illumination. The conductance for PNIPAM and CMC-coated ZnO NBs was increased by 100 and 15 times, respectively (see Supporting Information Figure S1). Surprisingly, the photoconductance of the PSS-coated ZnO NB (red line) increases by 75000 times when UV was on. This is a sharp contrast to the other three polymers-coated ZnO NBs. It should be noted that dry PSS polymer itself is nonconductive and showed almost no response to UV illumination (blue line), thus, on its own it cannot contribute to the huge increase in conductance. In contrast, PSS-coated ZnO NB showed a much smaller response (∼2) to the light of 523 and 680 nm wavelength (see Supporting Information Figure S2). This phenomenon shows that the huge increase in conductance for PSS-coated NB must be a coupling effect between the polymer and ZnO. This study shows the distinct effect of different polymers on the photoconductance of ZnO NB.

From our measurement data, coating of polymers normally increases the UV response of ZnO NB by 10−100 times. However, the UV response of PSS-coated NB has a much larger magnitude. To explore the reason for this distinct performance, we have measured the UV absorption spectra of the four polymers used in our study. As shown in Figure 1b, PS-co-MAc MA, PNIPAM, and CMC show a UV absorption peak at wavelengths around 190−200 nm. In the 280 nm wavelength range as provided by the UV source in our experiments, the three polymers show little absorption. However, as for the UV absorption spectrum of PSS, there are two absorption peaks around 190 and 260 nm, matching well to the excitation wavelength of the UV source. The data suggest that the large absorbance of the PSS to the UV is likely responsible for the observed huge increase in photoconductance.
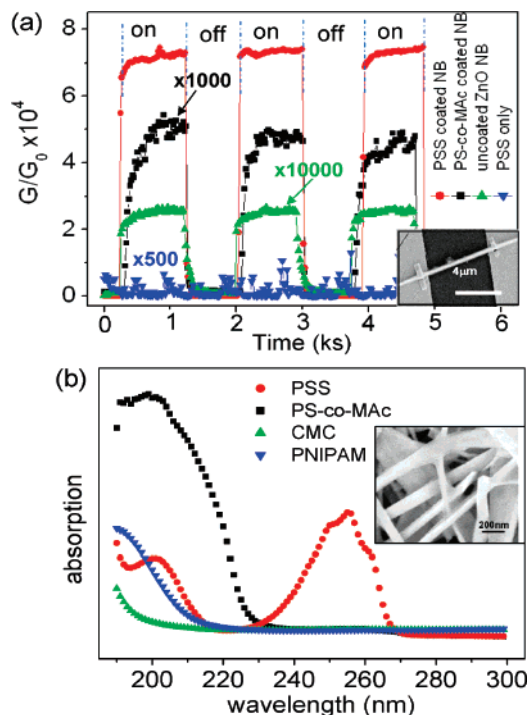
Figure 1. (a) Normalized conductance responses of a single functionalized ZnO NB device (see inset) upon UV illumination being tuned on and off: bare ZnO NB without coating (green line, magnified by 10000), PS-co-MAc-coated ZnO NB (dark line, magnified by 1000), PSS-coated ZnO NB (red line), PSS polymer only (blue line, magnified by 500). Inset is an SEM image of a typical device. The applied voltage remained at 1 V for all of the measurements. (b) UV absorption spectra of PSS (red line), PS-co-MAc (dark line), PNIPAM (blue line), CMC (green line). Inset is an SEM image of a polymer-coated ZnO NB sample.

Soci et al.[9] have proposed that the high sensitivity UV detection of ZnO NW was due to the presence of oxygen-related hole-trapping states at the NW surface. This process can also be applied to explain our observation. The first layer of coated polymer is cationically charged PDADMAC. The free electrons might be trapped by the positively charged sites at the surface. Upon UV illumination, these immobilized electrons can trap the photon-generated holes and thus reduce the electron−hole recombination rates in ZnO NB and increase the carrier lifetime. This mechanism accounts for the enhanced UV response for ZnO NB coated with PS-co-Mac, PNIPAM, and CMC.

The above mechanism may not be sufficient to account for the huge increase in photoresponse of the PSS-coated NBs. From Figure 1b, the UV absorption spectrum of PSS has a peak at around 260 nm, which is coincidently close to the applied UV source wavelength. We proposed that this absorption peak and the related molecular energy states in PSS play a significant role for enhancing the photon response. Although the first layer of ZnO NB surface is covered by PDADMAC, it is well-known that the monolayer adsorption usually cannot reach 100% coverage. Therefore, the remaining surface could be covered by the next adsorbed layer of PSS, as shown in Figure 2b. We now consider the area that PSS is directly interfacing with ZnO. Under UV light, an electron in PSS is excited from the ground-state energy state to an exited energy state owing to high absorption, which creates an unoccupied energy state (step 1). If the ground energy state of the PSS is at the level within the band gap of ZnO, it is possible that the electron in the valence band of ZnO NB is likely to be excited to the ground state of PSS, which subsequently transits to the conduction band of ZnO (step 2). This "hopping" process may largely enhance the transition probability of the valence electrons in ZnO to its conduction band, resulting in a large increase of electron−hole pairs (Figure 2a).
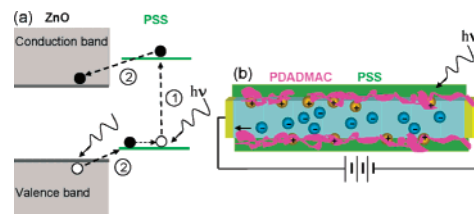

Figure 2. (a) Schematic illustration of the electron−hole generation process with facilitation of transition states from the molecular energy states in PSS. (b) Schematic illustration of photon-induced carrier transportation process in a ZnO NB by UV illumination.

The role played by PSS is to serve as a hopping-state or bridge for the electron transfer. As discussed above, the as generated holes are trapped at the NB surface by the PDADMAC, while the electrons are transported through the NB core, (Figure 2b). Therefore, the conjunction of electron−hole pair generation in ZnO with the assistance of PSS and surface-hole trapping effect by PDADMAC may largely prevent the electron−hole recombination, resulting in a huge increase in the photoconductance of PSS-coated ZnO NB.

In conclusion, by coating ZnO NB using a polymer that exhibits a large UV absorption peak, the UV induced photoconductance increases by 5 orders of magnitude. This huge increase in photoconductance is suggested owing to an electron−hole generation process as assisted by the energy states in the polymer. Therefore, with coating UV sensitive polymers, the UV response of ZnO NB was greatly enhanced. This study sets the foundation for increasing the sensitivity of UV detectors based on ZnO. The result suggests that, by selecting polymers with different wavelengths of UV absorption, UV detectors with a large range of wavelengths and super-high sensitivity can be fabricated using arrays of ZnO NWs and NBs functionalized using different polymers. This discovery can have outstanding applications in photonics and optoelectronics.

Supporting Information Available: UV response of PNIPAM and CMC-coated ZnO NBs. Response of PSS-coated ZnO NB to 523 and 680 nm wavelength. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Nakayama, Y.; Pauzauskie, P. J.; Radenovic, A.; Onorato, R. M.; Saykally, R. J.; Liphardt, J.; Yang, P. D. *Nature* **2007**, *447*, 1098.
(2) Pearton, S. J.; Norton, D. P.; Ip, K.; Heo, Y. W.; Steiner, T. *Prog. Mater. Sci.* **2005**, *50*, 293.
(3) Cha, S. N.; Jang, J. E.; Choi, Y.; Amaratunga, G. A. J.; Ho, G. W.; Welland, M. E.; Hasko, D. G.; Kang, D. J.; Kim, J. M. *Appl. Phys. Lett.* **2006**, *89*, 263102.
(4) Lao, C. S.; Liu, J.; Gao, P. X.; Zhang, L. Y.; Davidovic, D.; Tummala, R.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 263.
(5) Wang, Z. L. *Adv. Mater.* **2007**, *19*, 889.
(6) Wang, Z. L. *Mater. Today* **2007**, *10*, 20.
(7) Wang, X. D.; Song, J. H.; Liu, J.; Wang, Z. L. *Science* **2007**, *316*, 102.
(8) Wang, X. D.; Zhou, J.; Song, J. H.; Liu, J.; Xu, N. S.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 2768.
(9) Wang, Z. L.; Song, J. H. *Science* **2006**, *312*, 242.
(10) Soci, C.; Zhang, A.; Xiang, B.; Dayeh, S. A.; Aplin, D. P. R.; Park, J.; Bao, X. Y.; Lo, Y. H.; Wang, D. *Nano Lett.* **2007**, *7*, 1003.
(11) Lao, C. S.; Li, Y.; Wong, C. P.; Wang, Z. L. *Nano Lett.* **2007**, *7*, 1323.
(12) Park, W. I.; Kim, J. S.; Yi, G. C.; Bae, M. H.; Lee, H. J. *Appl. Phys. Lett.* **2004**, *85*, 5052.
(13) Khrenov, V.; Klapper, M.; Koch, M.; Mullen, K. *Macromol. Chem. Phys.* **2005**, *206*, 95.
(14) Lao, C. S.; Kuang, Q.; Wang, Z. L.; Park, M. C.; Deng, Y. L. *Appl. Phys. Lett.* **2007**, *90*, 262107.

JA075249W